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(54) Process for the preparation of Cotelomers of vinylidene fluoride with fluorinated olefins.

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Description

The present invention relates to cotelomers of vinylidene fluoride with fluorinated olefins containing at least one terminal bromine or iodine atom, useful as plasticizing additive in fluoroelastomeric compositions, which are peroxy-curable.

In the technical literature processes are known for preparing homotelomers of $CH_2=CF_2$ by the action of telogen agents. Also known are copolymers of $CF_2=CH_2$ with fluorinated olefins, obtained in the presence of halogenated telogen agents (JP-A- 73-96684 and 84-20310) corresponding to EP-A-101930. In the known processes, said telogens, which behave as chain transfer agents, are used in amounts not higher than 10% by weight based on the polymer weight. Thus, polymeric products are obtained, which have a molecular weight not lower than 8000.

The object of the present invention is the preparation of cotelomers of vinylidene fluoride with at least one further fluorinated olefin, carried out by using free-radical polymerisation initiators and a telogen agent belonging to the class of bromoalkanes and iodoalkanes, in an amount at least equal to 10% by mol relatively to the total monomer mols; the telogen can be also used in high amounts, e.g. of 100%. In these cases, the telogen is also used as the solvent medium.

The so-obtained telomers are novel products having the general formula:

$$R\,[(CF_2CH_2)n\,(C_3F_6)m\,(C_2F_4)p\,(C_2F_3Cl)q]\,X \qquad (I)$$

wherein X is either Br or I, the units with n, m, p, q indices are randomly distributed along the telomer chain, R is a linear or branched C_1-C_{20} alkyl radical which can also contain halogens and also ester or ether groups, and wherein:

n is an integer comprised within the range of from 1 to 30,

m is an integer comprised within the range of from 0 to 10,

p and q are integers comprised within the range of from 0 to 20,

with the proviso that m + p + q is at least 1, said cotelomers having a molecular weight lower than 8000.

Obviously, the telomerization product can be practically constituted also by a mixture of individual cotelomers having different n, m, p, q indices (in the examples, the average values are reported).

These products find an interesting use as additives in fluoroelastomeric peroxy-curable compositions due to their action as plasticizers and to the improvement of the low-temperature properties of the cured article, and to their property of co-vulcanizing with the base fluoroelastomer in the presence of a curing agent of peroxidic type. Furthermore, they are useful for improving compatibility of fluoroelastomers with non-fluorinated elastomers.

The preparation of the cotelomers according to the invention is carried out by reacting vinylidene fluoride with one or more of the fluorinated olefins indicated in the general formula (I) in the presence of a free-radical polymerization initiator and of a telogen having the general formula RX, wherein X is either Br or I, and R is a radical belonging to the type as indicated in the general formula (I), at a temperature comprised within the range of from 0 to 200 °C. The telomerization is carried out in a liquid phase, constituted by the telogen, containing the monomers, in the presence or absence of an inert solvent.

As suitable telogens, there can be used: dibromodifluoromethane, 1,2-dibromotetrafluoroethane, trifluoromethyl iodide, bromotrichloromethane, 1-bromo-perfluorobutane, 2-bromo-propane, ter-butyl bromide.

As free-radical initiators, all those are suitable, which are well-known in the free-radical polymerization, such as the peroxides and azo-compounds. Among the peroxides, in particular, di-tert-butylperoxide, benzoylperoxide, di-cumylperoxide, bis-peroxy-carbamates and bis-peroxy-carbonates are preferred.

The amount of free-radical initiator relatively to the total sum of fluorinated olefins is comprised within the range of from 0.01% by mol to 10%, preferably of from 1% to 5%.

As examples of cotelomers according to the invention, those can be mentioned, which have the composition, as referred only to the telomerized olefins:

- $CH_2=CF_2$: from 10% to 90% by mol;
- C_3F_6 : from 0 to 45% by mol;
- C_2F_4 : from 0 to 90% by mol;
- $CClF=CF_2$: from 0 to 90% by mol.

The telomers having composition:

- $CH_2=CF_2$: from 50% to 90% by mol;
- C_3F_6 : from 0 to 25% by mol;
- C_2F_4 : from 10 to 50% by mol;

$CClF=CF_2$: from 10 to 50% by mol.

are preferred.

Any person skilled in the art will be able to select the operating conditions for obtaining the cotelomer having the desired composition.

For example, for obtaining a cotelomer having an average number molecular weight 1000, with the composition, as % by mol of:

VDF = 75; TFE = 25

the process is carried out in the presence of peroxides with a VDF/TFE molar ratio of 72/28, at a temperature of 140° C, and with a telogen/monomers ratio = 0.3 (telogen = CF_2Br-CF_2Br), by interrupting the reaction when the conversion rate has reached 30%.

The cotelomers of the invention have demonstrated to be endowed with a higher thermal stability than the corresponding $CF_2=CH_2$ homotelomers. Furthermore, contrary to what one could suppose, they have a very low T_g, practically of the same order as of a $CF_2=CH_2$ homotelomer having the same molecular weight.

To the purpose of illustrating the process and the products according to the invention, there are reported characteristics of $CF_2=CH_2/C_2F_4$ (VDF/TFE) cotelomers, obtained at 150° C with 10 mol % of CF_2Br-CF_2Br telogen, during a 3-hour reaction time (for comparative purposes, also the characteristics of a VDF homotelomer are shown).

Composition, Monomers in Reaction	Composition, Monomers in Product	Polymerization Degree n + p	T_g
VDF = 100%	100%	12	- 85° C
VDF = 100%	100%	16	- 80° C
VDF/TFE = 90/10	85/15	16	- 84° C
VDF = 100%	100%	20	- 72° C
VDF/TFE = 70/30	73/27	21	- 83° C

Such a result as reported in the above table is completely unexpected, because the introduction of the perfluorinated TFE, should lead to a further T_g increase, due to the increased chain rigidity, as it is observed in $CH_2=CF_2$ copolymers.

For example in the case of Tecnoflon® NM copolymer having the following composition: $CH_2=CF_2$ 80%, C_3F_6 20% a Tg = 23° C is observed, while in Tecnoflon® T terpolymer having composition $CH_2=CF_2$ 62%, C_3F_6 20%, TFE 18%, the Tg increases to -17° C. The introduction in polymer chain of TFE units in an amount of 18% leads to an increase of Tg = +6° C.(Bonardelli, Moggi, Turturro Polymer 1986 vol. 27, page 905). In the copolymers of the present invention it is not observed such a Tg increase (see Examples 2 and 2A).

The use of these cotelomers is described in EP-A-251 285.

For illustrative purposes, the following examples of practical embodiments of the invention are reported.

EXAMPLE 1

Into an AISI-316, 500-ml autoclave, 220.5 g of CF_2Br-CF_2Br and 0.5 g of di-tert.butylperoxide are charged. 8.3 g of VDF and 6.0 g of PFP (C_3F_6) are then charged. The temperature is brought under stirring for 3 hours to 150° C, and the mass is allowed to react. The autoclave is cooled to room temperature. The CF_2Br-CF_2Br excess is removed by distillation. The remaining product was characterized by N.M.R. Spectrometry and elemental analysis; its osmometric average number molecular weight (M_n), average composition and glass transition temperature (T_g) were determined.

The results obtained are:

Br = 24% by weight; $\overline{M}_n$ = 660; n = 4.2; m = 0.8; T_g = -94° C; C_3F_6 % = 16% by mol.

EXAMPLE 2

Th preparation is carried out by operating according to th working conditions of Example 1, but at 140° C, using 363.3 g of CF_2Br-CF_2Br, 0.82 g of di-tert.butylp roxide, 12.8 g of VDF, 8.3 g of PFP and 2.5 g of TFE.

The results obtained are:

Br = 21% by weight; $\overline{M}_n$ = 730; the average values of n and m are: n = 4.5, m = 1.1., p = 1.2; T_g =

-92° C:

EXAMPLE 2A

Operating according to the same working conditions, but with 14.4 g of VDF, 8.3 g of PFP and in complete absence of TFE; a polymer having T_g = -90° C is obtained.

EXAMPLE 3

The preparation is carried out by operating according to the working conditions of Example 1, but at 140° C, using TFE instead of PFP. To the autoclave 428.4 g of CF_2Br-CF_2Br, 19.3 g of di-tert.butylperoxide, 19.2 g of VDF, and 3 g of TFE were charged.

The results obtained are:

Br = 22.9% by weight, $\overline{M}_n$ = 690; n = 5; p = 1; T_g = -102° C.

EXAMPLE 4

The preparation is carried out by operating according to the modalities of Example 3, using 0.96 g of di-tert.butylperoxide, and by interrupting the test after 2 hours.

The results obtained are:

Br = 21.1% by weight; $\overline{M}_n$ = 730, n = 5.8, p = 1.1, T_g = -106° C.

EXAMPLE 5

The preparation is carried out by operating according to the working conditions of Example 1, but at T = 145° C, by using 102 g of CF_2Br-CF_2Br, 1.14 g of di-tert.butylperoxide, 19.2 g of VDF and 13.5 g of PFP.

The results obtained are:

$\overline{M}_n$ = 940; n = 5.8; m = 2.1; T_g = -92° C.

EXAMPLE 6

The preparation is carried out by operating according to the working conditions of Example 1, using 16.8 g of CF_2Br-CF_2Br, 1.30 g of di-tert.butylperoxide, 32 g of VDF and 22.5 of PFP.

The results obtained are:

Br = 5.1% by weight, $\overline{M}_n$ = 3100, n = 28, m = 7.1, T_g = -30° C.

EXAMPLE 7

The preparation is carried out by operating according to the working conditions of Example 6, using 5.25 g of PFP.

The results obtained are:

$\overline{M}_n$ = 2900, n = 27, m = 2.5, T_g = -94° C.

EXAMPLE 8

The preparation is carried out by operating according to the modalities of Example 6, using 50.7 g of CF_2Br-CF_2Br.

The results obtained are:

$\overline{M}_n$ = 1200, n = 11.2, m = 2.1, T_g = -74° C.

EXAMPLE 9

The preparation is carried out by operating according to the working conditions of Example 4, using 85.8 g of CF_2Br-CF_2Br.

The results obtained are:

$\overline{M}_n$ = 900, n = 7.4, p = 1.2, T_g = -109° C.

EXAMPLE 10

The preparation is carried out by operating according to the working conditions of Example 9, using 25.7 g of CF_2Br-CF_2Br.

The results obtained are:

$\overline{M}_n$ = 950, $\underline{n}$ = 8.9, $\underline{p}$ = 1.1, T_g = 100° C.

EXAMPLE 11

The preparation is carried out by operating as in Example 3, using 30.4 g of CF_2Br-CF_2Br, 20 g of VDF and 9 g of C_2F_4, 1.1 g of di-tert.butylperoxide. The reaction mass is heated 1 hour at 130° C.

The product obtained has an average number molecular weight ($\overline{M}_n$), measured by osmometry, of 1,400. T_g = -90° C.

EXAMPLE 12

The preparation is carried out by operating as in Example 1, but with 101.5 g of CF_2Br - CF_2Br, using as the peroxidic initiator Perkadox® 16 (di-4,4'-tert-butyl-cyclohexyl-peroxydicarbonate) 2.7 g , charging 19.2 g of VDF and 9 g of TFE. The reaction mass has been heated for 2 hours at 62° C.

The results obtained are:

$\overline{M}_n$ = 1.300, $\underline{n}$ = 11.2, $\underline{p}$ = 3.1, T_g = -86° C.

EXAMPLE 13

Into the apparatus as described in Example 6, 20.4 g of CF_2Br-CF_2Br, 0.9 g of di-tert-butylperoxide, 7 g of chlorotrifluotoethylene and 13 g of vinylidene fluoride are charged. The temperature is increased to 130° C and has been maintained at this value for 150 minutes. The product is separated as described in Example 1. The average number of molecular weight ($\overline{M}_n$) results equal to 1,200, $\underline{n}$ = 10.1, q = 3, T_g = -65° C.

Claims

1. Cotelomers of vinylidene fluoride with fluorinated olefins, having the general formula:

$$R\,[(CF_2CH_2)n\,(C_3F_6)m\,(C_2F_4)p\,(C_2F_3Cl)q]\,X \qquad (I)$$

wherein X is either Br or I, the units with n, m, p, q indices are randomly distributed along the telomer chain, R is a linear or branched C_1-C_{20} alkyl radical which can also contain halogen and optionally ester or ether groups, and wherein:
n is an integer comprised within the range of from 1 to 30,
m is an integer comprised within the range of from 0 to 10,
p and q are integers comprised within the range of from 0 to 20,
with the proviso that m + p + q is at least 1, said cotelomers having a molecular weight lower than 8000.

2. Cotelomers according to claim 1, wherein the composition, as referred to the telomerized olefins only,is as follows:

$CH_2=CF_2$	: from 10 to 90% by mol;
C_3F_6	: from 0 to 45% by mol;
C_2F_4	: from 0 to 90% by mol;
$CClF=CF_2$	: from 0 to 90% by mol.

3. Cotelomers according to claim 2, wherein the composition is as follows:

$CH_2=CF_2$	: from 50 to 90% by mol;
C_3F_6	: from 0 to 25% by mol;
C_2F_4 and C_2F_3Cl	: from 10 to 50% by mol.

4. A process for the preparation of the cotelomers of claim 1 which comprises reacting vinylidene fluorid with one or more of the fluorinat d olefins as indicated in formula I, at a temperature of from 0 to 200° C in the presenc of a free-radical polymerization initiator and of a telogen having the general formula RX, wherein X and R are as defined in claim 1, said telogen being used in an amount of at

least 10% by mol relatively to the total monomer mols.

5. The process of claim 4 wherein the free-radical initiator is used in an amount of from 0.01 to 10% by mol, referring to the total sum of the olefins to be polymerised.

6. The process of claim 5 wherein the free-radical initiator is used in an amount of from 1 to 5% by mol.

Revendications

1. Cotélomères de fluorure de vinylidène et d'oléfines fluorées, représentés par la formule générale :

$$R\,[(CF_2CH_2)_n(C_3F_6)_m(C_2F_4)_p(C_2F_3Cl)_q]X \quad (I)$$

dans laquelle X est un atome de brome ou d'iode, les unités avec les indices n, m, p, q sont distribuées de façon aléatoire le long de la chaîne du télomère, R est un groupe alkyle en C_{1-20} à chaîne droite ou ramifiée qui peut aussi contenir des atomes d'halogène et aussi des groupes ester ou éther, et dans laquelle:
n est un entier compris dans la gamme de 1 à 30,
m est un entier compris dans la gamme de 0 à 10,
p et q sont des entiers compris dans la gamme de 0 à 20,
à condition que m+p+q soit au moins égal à 1, ces cotélomères ayant un poids moléculaire inférieur à 8000.

2. Cotélomères suivant la revendication 1, dans lesquels la composition en référence aux oléfines télomérisées uniquement, est la suivante:

$CH_2=CF_2$	de 10 à 90% en moles;
C_3F_6	de 0 à 45% en moles;
C_2F_4	de 0 à 90% en moles;
$CClF=CF_2$	de 0 à 90% en moles.

3. Cotélomères suivant la revendication 2, dans lesquels la composition est la suivante:

$CH_2=CF_2$	de 50 à 90% en moles;
C_3F_6	de 0 à 25% en moles;
C_2F_4 et C_2F_3Cl	de 10 à 50% en moles;

4. Un procédé pour la préparation des cotélomères suivant la revendication 1, qui comprend la réaction du fluorure de vinylidène avec une ou plusieurs des oléfines fluorées telles qu'indiquées dans la formule (I), à une température de 0 à 200 °C en présence d'un initiateur de polymérisation par radicaux libres et d'un télogène ayant la formule générale RX, dans laquelle X et R sont tels que définis dans la revendication 1, ce télogène étant utilisé en une quantité d'au moins 10% en moles par rapport au moles totales de monomères.

5. Le procédé suivant la revendication 4, dans lequel l'initiateur de radicaux libres est utilisé en une quantité de 0,01 à 10% en moles par rapport à la somme totale des oléfines devant être polymérisées.

6. Le procédé suivant la revendication 5, dans lequel l'initiateur de radicaux libres est utilisé en une quantité de 1 à 5% en moles.

Patentansprüche

1. Cotelomere von Vinylidenfluorid mit fluorierten Olefinen, die die allgemeine Formel

$$R\,[(CF_2CH_2)n\,(C_3F_6)m\,(C_2F_4)p\,(C_2F_3Cl)q]\,X \quad (I)$$

aufweisen,
worin X entweder Br oder I ist, die Einheiten mit den Indices n, m, p und q statistisch entlang der Telomer-Kette verteilt sind, R einen geradkettigen oder verzweigten $\overline{C}_1$-$\overline{C}_{20}$-Alkylrest darstellt, der auch Halog n und gegebenenfalls Ester- oder Ethergruppen enthalten kann, und worin

n eine ganze Zahl im Bereich von 1 bis 30 ist,
m eine ganze Zahl im Bereich von 0 bis 10 ist,
p und q ganze Zahlen im Bereich von 0 bis 20 sind,
mit der Maßgabe, daß m + p + q mindestens 1 ist,
wobei die Cotelomere ein Molekulargewicht niedriger als 8000 aufweisen.

2. Cotelomere nach Anspruch 1, worin die Zusammensetzung, lediglich auf die telomerisierten Olefine bezogen, wie folgt ist:

$CH_2 = CF_2$	: 10 bis 90 Mol-%
C_3F_6	: 0 bis 45 Mol-%
C_2F_4	: 0 bis 90 Mol-%
$CClF = F_2$	: 0 bis 90 Mol-%

3. Cotelomere nach Anspruch 2 mit der folgenden Zusammensetzung:

$CH_2 = CF_2$	: 50 bis 90 Mol-%
C_3F_6	. 0 bis 25 Mol-%
C_2F_4 und C_2F_3Cl	: 10 bis 50 Mol-%

4. Verfahren zur Herstellung der Cotelomere nach Anspruch 1, umfassend das Umsetzen von Vinylidenfluorid mit einem oder mehreren der fluorierten Olefine, wie in Formel I angegeben, bei einer Temperatur von 0 bis 200 °C in Gegenwart eines Radikal-Polymerisationsinitiators und eines Telogens der allgemeinen Formel RX, worin X und R wie in Anspruch 1 definiert sind, wobei das Telogen in einer Menge von mindestens 10 Mol-%, bezogen auf die Gesamtmole der Monomeren, eingesetzt wird.

5. Verfahren nach Anspruch 4, worin der Radikalinitiator in einer Menge von 0,01 bis 10 Mol-%, bezogen auf die Gesamtmenge der zu polymerisierenden Olefine, eingesetzt wird.

6. Verfahren nach Anspruch 5, worin der Radikalinitiator in einer Menge von 1 bis 5 Mol-% eingesetzt wird.